2950 Niles Road, St. Joseph, MI 49085-9659, USA
269.429.0300 fax 269.429.3852 hq@asabe.org www.asabe.org

An ASABE Meeting Presentation

Paper Number: 096758

Potential of Summer Legumes for Thermochemical Conversion to Synthetic Fuel

Keri B. Cantrell

USDA-ARS, Coastal Plains Research Center, 2611 W. Lucas St., Florence, SC 29501. keri.cantrell@ars.usda.gov.

Philip J. Bauer

USDA-ARS, Coastal Plains Research Center, Florence, SC. phil.bauer@ ars.usda.gov

Kyoung S. Ro

USDA-ARS, Coastal Plains Research Center, Florence, SC. kyoung.ro@ars.usda.gov

Written for presentation at the
2009 ASABE Annual International Meeting
Sponsored by ASABE
Grand Sierra Resort and Casino
Reno, Nevada
June 21 – June 24, 2009

***Abstract*.** Summer legumes are commonly used worldwide in crop rotations as a nitrogen source. One particular legume, sunn hemp (*Crotolaria juncea*), is a fast growing, high biomass yielding, tropical legume that may be a possible southeastern bioenergy crop. When comparing this legume to a commonly grown summer legume—cowpeas, sunn hemp was superior in biomass yield (kg ha^{-1}) and subsequent energy yield (GJ ha^{-1}). Interlinked with energy yield, the sunn hemp energy content (MJ kg^{-1}) at the greatest maturity sampled (after 12 weeks) was 19.0 MJ kg^{-1}. This was 6% greater than that of cowpeas. Even though sunn hemp had a greater amount of ash, plant nutrient concentrations were lower in some cases of minerals (K, Ca, Mg, S) known to reduce thermochemical conversion process efficiency. Pyrolytic degradation of both legumes revealed that sunn hemp began to degrade at higher temperatures as well as release more volatile matter. This volatile matter would be amenable to downstream conversion processes to generate either heat or synthetic fuels.

Keywords. Bioenergy, energy conversion, thermogravimetric analysis, thermal analysis, crop production

Introduction

Demand for renewable bioenergy feedstocks has grown and developed worldwide with prominent crops being corn, sugarcane, and soybean. Alongside this increase are concerns over the sustainable use of current land and water resources as well as distribution of these resources to provide both food and fuel. One way to ease the strain on natural resources is to maximize the annual productivity of agricultural lands by establishing rotational cropping systems that include both food/feed/fiber crops and energy crops. Summer legumes planted during fallow periods prior to a cash crop may not only be used as a nitrogen source but also as a bioenergy feedstock. One such summer legume, sunn hemp (*Crotolaria juncea*), is a fast growing legume capable of accumulating large amounts of biomass in a short time frame. During a three-year study, sunn hemp biomass accumulation within a 9 to 12 week growing period averaged 5.9 Mg ha^{-1} (Mansoer et al., 1997) This biomass along with other agricultural residues can be converted thermochemically into combustible gases, bio-oils, or biochar. These by-products can supplement other energy sources.

The objective of this investigation was to assess differences in two legumes sunn hemp and cowpeas, a commonly grown legume, with regards to biomass and bioenergy production. Specifically, this was accomplished by evaluating: 1) biomass yield; 2) energy density; 3) energy yield; 4) measured plant nutrients; and 5) pyrolytic degradation characteristics.

Methods

Plant Materials and Energy Production

Sunn hemp and cowpeas (Figure 1) were grown in replicate plots (12 m x 15 m) near Florence, SC in 2004 and 2006. In 2004, the legumes were grown on Nobocco loamy sand. In 2006, the legumes were grown on Bonneau sand. The legume plots were established in late July each year. An experiment was established in 2005-2006, but dry soil conditions following summer legume planting resulted in poor stands. No pest control measures were used in growing the legumes.

Legume biomass was harvested three times in both 2004 (26 August, 1 October, and 5 November) and 2006 (30 August, 29 September, and 25 October). The last biomass collection of each season was made right after the first killing freeze of the fall. Legume biomass yields within each plot were determined by collecting 0.57 m^2 areas. After collection, samples were placed in a 65 °C oven until dry and then weighed. A portion of dried legume samples were ball milled and analyzed for energy density or higher heating value (HHV) using a LECO AC500 Isoperibol Calorimeter (Leco Corp., St. Joseph, MI) following ASTM Standard D5865 (ASTM, 2006). Subsequent legume energy yields (E_{ha}) were calculated as the product of the energy density and biomass yield.

Figure 1. Sunn hemp (left) and cowpeas (right) about 6 weeks after planting.

Plant Tissue Characterization

Dried and milled grass samples were analyzed for the following nutrients: phosphorous (P); potassium (K); calcium (Ca); magnesium (Mg); sulfur (S); zinc (Zn); copper (Cu); manganese (Mn); iron (Fe); and sodium (Na). Plant nutrient analyses by inductive coupled plasma (ICP) were provided by the Agricultural Service Laboratory at Clemson University and conducted following general procedures outlined elsewhere (Peters et al., 2003). Samples were also subjected to a proximate analysis that yielded a biomass sample's ash, volatile matter and fixed carbon contents. These components were determined using a thermogravimetric analyzer (TGA; Model TGA/SDTA851e, Mettler Toledo International Inc., Columbus, OH) following the same temperature programs referenced in ASTM D3172 (ASTM, 2006).

Thermal Analysis

Pyrolytic experiments were conducted on each harvested sample (n = 4) using the TGA where the mass loss (thermogravimetry, TG) and temperature changes (differential thermal analysis, DTA) are recorded simultaneously. This unit operated under a three-point calibration using Indium, Aluminum, and Gold. All samples were placed in an AlO_3 70μl crucible and pyrolyzed in UHP N_2 atmosphere at a flow rate of 60 ml min^{-1} at a constant heating rate of 20 C° min^{-1} within the temperature range of 40 to 800°C.

Statistical Analysis

Data were analyzed by Proc GLM (General Linear Model) and LSD (least significant difference) with Version 9.2 of Statistical Analysis System (SAS Institute Inc., Cary, NC). Significant differences between legumes were based on F-test ($P < 0.05$).

Results and Discussion

Energy Production and Plant Tissue Characterization

Sunn hemp and cowpea energy densities (MJ kg^{-1}) and yields (MJ ha^{-1}) were analyzed for statistical differences by year due to differences in type of soil as well as rainfall. Rainfall accumulation totaled 56 cm in 2004 and 22 cm in 2006 (Bauer et al., 2009). The ample rainfall in 2004 benefited sunn hemp growth resulting in a 3 month biomass yield of almost 11,000 kg ha^{-1}. This was almost twice the biomass accumulated by that reported by Mansoer et al. (1997) as 5.9 Mg ha^{-1}. The limited rainfall for 2006 and plant growth on a more droughty soil resulted in lower total biomass (Bauer et al., 2009). During this time, there was no significant difference in biomass yield for the two species at any sampling time.

Table 1. Biomass, energy content (HHV), and energy yield at various months after planting (MAP) for sunn hemp (SH) and cowpeas (CP).

		Biomass			HHV			Energy Yield		
		MAP								
Year	Legume	1	2	3	1	2	3	1	2	3
		-----kg ha^{-1} ------			-----MJ kg^{-1}-----			-----GJ ha^{-1}-----		
2004	SH	2070	7891	10718	17.89	18.73	19.00	37.0	147.8	203.6
	CP	1628	3222	---	18.19	17.85	---	29.6	57.4	---
	Prob.>F	0.15	0.01	---	0.04	0.001	---	0.18	0.002	---
2006	SH	1264	6973	7253	19.27	18.81	18.87	24.3	131.1	137.0
	CP	1683	5507	5909	18.16	17.86	17.81	30.5	98.3	105.2
	Prob.>F	0.19	0.11	0.20	0.000	0.000	0.000	0.28	0.057	0.12

For both years, sunn hemp after 2 months of planting was more energy dense than the cowpeas with an HHV 5 to 6% greater (Table 1). Cowpea HHV ranged from 17.81 to 18.19 MJ kg^{-1} while sunn hemp HHV ranged from 17.89 to 19.27 MJ kg^{-1}. For the case of sunn hemp, these energy densities were greater than the HHV reported for both switchgrass by Boateng et al. (2007) as 18.57 MJ kg^{-1} and bermudagrass by Cantrell et al. (2009) as 18.78 MJ kg^{-1}. For the case of sunn hemp grown on Nobocco sand with ample rainfall in 2004, the HHV increased with biomass production. However, for sunn hemp harvested on Bonneau sand in 2006 under limited rainfall, the sunn hemp HHV decreased with plant age in accordance to increases with the ash component (Table 2). These phenomena may be attributed to physiological adaptations of the plants—during water-deficit stress conditions, plants shed leaves leaving behind the stalk or stem that has greater ash content than leaves. This explanation is further supported by both plants having little biomass accumulation during the third month of growth.

Table 2. Volatile matter (VM), fixed carbon (FC), and ash compositions at various months after planting (MAP) of sunn hemp (SH) and cowpeas (CP).

Year	Legume	MAP	VM		FC[a]		Ash	
					---------wt%$_{db}$--------			
2004	CP	1	67.92	(1.60)	15.82	(2.82)	15.08	(4.16)
		2	70.10	(1.73)	19.88	(3.74)	9.59	(2.62)
	SH	1	64.76	(1.69)	25.91	(5.49)	9.45	(3.17)
		2	65.31	(2.93)	21.89	(4.89)	12.84	(2.43)
		3	72.07	(3.58)	14.22	(4.71)	14.82	(4.23)
2006	CP	1	70.31	(1.88)	18.19	(0.67)	11.49	(1.72)
		2	72.96	(2.44)	22.25	(2.83)	4.79	(2.66)**
		3	69.09	(0.19)**	22.70	(0.66)	8.21	(0.81)**
	SH	1	72.66	(4.32)	16.01	(3.34)	11.94	(1.47)
		2	69.81	(0.78)	15.86	(3.38)	13.61	(2.60)
		3	64.98	(1.92)	22.44	(1.66)	13.51	(1.63)

[a] Fixed carbon calculated as 100 – VM – Ash; ** statistically different from SH counterpart

In addition to a greater HHV, the sunn hemp had a significantly greater energy yield ranging from 131 to 204 GJ ha^{-1}. Despite sunn hemp yielding significantly greater HHV than cowpeas in 2006, the overall energy yields were not different. However, for 2004 the significant sunn hemp growth after 2 months along with greater HHV resulted in significantly greater energy yields—almost 2.5 times the growth. Growth of sunn hemp over cowpeas would provide more energy for a local combustion plant—between 30 and 150%. With the increase in available energy per area, a larger power plant can be supported (Figure 2). Assuming 40% electrical conversion efficiency (Demirbas, 2001), sunn hemp grown within a 35 km (~22 mi) radius (i.e., harvested from 3848 km^2 area) would provide 1 MW. To obtain this power from cowpeas, the radius would need to expand to 56 km (9967 km^2 area).

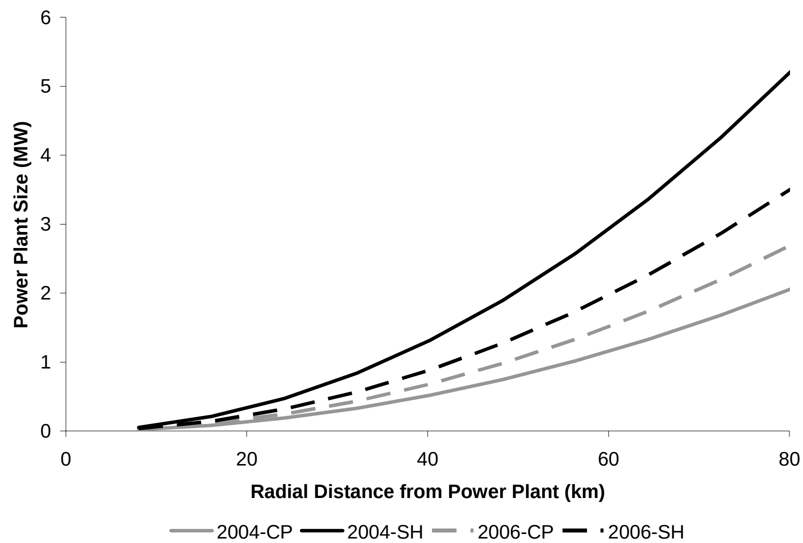

Figure 2. Relative power plant size* supported by combustion of sunn hemp (SH) and cowpeas (CP) grown in 3 months within defined radius. *Calculations assume 40% conversion efficiency and 40% increase in CP biomass during third month.

Among the measured plant nutrients (Tables 3 and 4), K was the most significant mineral present with concentrations upwards of 3.13 $wt\%_{db}$ for cowpeas and 2.92 $wt\%_{db}$ for sunn hemp. Plant Ca, Mg, and P were also present in relatively large quantities. Plant Cu concentrations were the lowest of measured nutrients ranging from 6.00 to 17.8 ppm. All plant nutrient concentrations decreased with growth. Few nutrient concentration differences ($\alpha = 0.05$) were noted between cowpeas and sunn hemp. When differences were noted, cowpeas consistently had greater concentrations of those nutrients. The one exception was for Na. Plant nutrient concentrations at time of harvest would be greater for cowpeas for K, Mg, S, and Zn. This results in 3 to 28% more mass (kg ha^{-1}) of these nutrients being removed and potentially residing in the residual combustion ash portion. In addition, the exact role these minerals play is unknown during thermochemical conversion.

During pyrolysis and gasification, the inorganic components K, Ca, and Na are thought to act as catalysts improving the rate of degradation and conversion efficiency. Inorganic salts have been shown to reduce the onset temperature for degradation as well as increase gaseous volatiles (Williams and Horne, 1994; Raveendran et al., 1995). Additionally, both K and Na have been identified to promote the secondary char gasification reactions with CO_2 and H_2O that generate the combustible gases of CO and H_2 (Raveendran and Ganesh, 1996). These components (CO and H_2) positively influence the caloric value of the gas. However, the removal of precipitating minerals like Ca, Mg, and P as well as S may be necessary as these have been identified as poisoning metal catalysts used in catalytic driven gasification processes (Ro et al. 2007). Thus, developing a quality bioenergy feedstock for gasification or pyrolysis where a combustible gas or oil is desired will require a balance among minerals.

Table 3. Major plant nutrient concentrations at various months after planting (MAP) of sunn hemp (SH) and cowpeas (CP).

Year	Legume	MAP	P		K		Ca		Mg		S	
						------------------------wt%$_{db}$	-----------------------					
2004	CP	1	0.38	(0.01)**	3.13	(0.68)	1.18	(0.10)**	0.47	(0.03)	0.22	(0.05)
		2	0.23	(0.02)	2.23	(0.34)**	0.49	(0.13)	0.29	(0.02)	0.19	(0.03)**
	SH	1	0.31	(0.05)	2.92	(0.46)	0.73	(0.17)	0.38	(0.09)	0.20	(0.04)
		2	0.25	(0.03)	1.54	(0.24)	0.78	(0.27)	0.38	(0.09)	0.14	(0.01)
		3	0.24	(0.04)	1.33	(0.23)	0.62	(0.20)	0.33	(0.07)	0.13	(0.03)
2006	CP	1	0.32	(0.05)	2.92	(0.46)	1.15	(0.15)**	0.58	(0.09)	0.24	(0.02)
		2	0.18	(0.05)	1.22	(0.14)	0.81	(0.33)	0.39	(0.01)	0.13	(0.02)
		3	0.16	(0.03)	1.25	(0.17)**	0.57	(0.12)	0.44	(0.03)**	0.15	(0.01)**
	SH	1	0.35	(0.08)	2.52	(0.13)	0.78	(0.20)	0.49	(0.09)	0.21	(0.03)
		2	0.19	(0.01)	1.25	(0.06)	0.58	(0.04)	0.37	(0.04)	0.11	(0.02)
		3	0.14	(0.02)	0.88	(0.15)	0.45	(0.11)	0.33	(0.08)	0.09	(0.02)

** Statistically different from SH counterpart

Table 4. Minor plant nutrient concentrations at various months after planting (MAP) of sunn hemp (SH) and cowpeas (CP).

Year	Legume	MAP	Zn		Cu		Mn		Fe		Na	
						------------------------ppm	-----------------------					
2004	CP	1	50.3	(7.63)**	8.25	(1.71)	95.5	(18.1)**	104.8	(8.22)**	40.8	(5.44)
		2	42.0	(3.74)**	6.50	(0.58)	72.5	(9.68)	66.8	(20.7)	60.8	(6.55)
	SH	1	38.3	(3.77)	6.00	(0.82)	44.5	(11.2)	72.8	(20.6)	43.0	(10.8)
		2	32.3	(0.96)	9.25	(4.57)	56.0	(9.56)	56.0	(7.39)	45.8	(12.0)
		3	32.5	(5.20)	6.50	(1.00)	38.8	(10.3)	47.0	(13.7)	21.5	(5.20)
2006	CP	1	47.3	(6.55)	17.8	(7.80)	64.8	(10.3)**	174.0	(58.1)	33.0	(6.38)
		2	42.8	(13.1)	6.00	(2.45)	52.0	(31.9)	65.0	(26.7)	19.0	(2.83)**
		3	51.0	(7.87)**	5.50	(1.29)	38.3	(7.50)	49.3	(9.91)	32.8	(8.42)
	SH	1	36.3	(7.85)	13.3	(2.63)	43.0	(9.31)	101.3	(14.4)	35.3	(10.2)
		2	30.3	(8.14)	7.50	(2.52)	36.5	(6.03)	50.5	(10.8)	29.8	(8.06)
		3	29.8	(10.6)	6.75	(0.50)	29.0	(7.39)	42.0	(19.1)	23.0	(8.91)

** Statistically different from SH counterpart

Thermal Analysis

The weight loss (TG) and derivative (DTG) curves of the plants (Fig. 3) exhibited typical pyrolytic degradation profiles of other plant materials (Biagini et al., 2006; Kumar et al., 2008). After drying, samples underwent a primary devolatilization stage. The onset temperature of this stage was determined as the weight loss of 5% respect to the final dry-basis weight loss. Once the bulk of biomass was removed, the next stage was a slow and continuous weight loss. This weight loss has been attributed to the degradation of heavier chemical structures in the plant matrix (Biagini et al., 2006). Some of these materials may be native to the plant structure or produced during the primary pyrolysis stage, sometimes referred to as “secondary thermolysis” (Fisher et al., 2002). A final temperature of primary devolatilization was defined on the DTG curve as the temperature corresponding to the intersection of tangent lines in both devolatilization stages. Comparing the two stages, the primary devolatilization stage released more volatile matter that can be used in combustion systems or converted into higher-value fuels (Table 5).

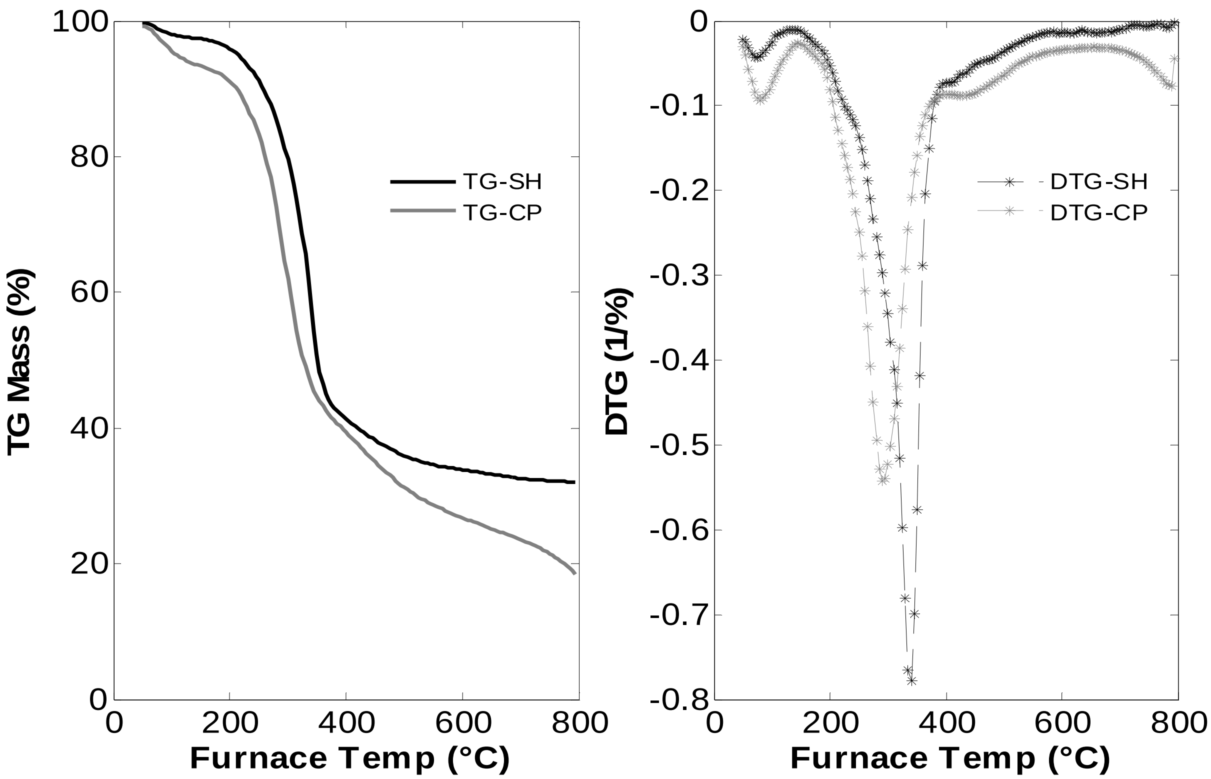

Figure 3. Thermogravimetric characterization (*n* = 3) of the pyrolysis of sunn hemp (SH) and cowpeas (CP) three months after planting. (TGA Method: 40 – 800°C; 20 °C min^{-1}; N_2 atmosphere)

For this current study, the temperature for the onset of devolatilization (T_{on}) was higher for sunn hemp and ranged between 200 and 229°C (Table 5; Figure 3). Additionally, T_{on} was observed to increase with the age and physiological changes of the plant. The same was true for the end temperature of the primary devolatilization stage—T_p (Table 5; Figure 4). However, the temperature range for primary devolatilization among the two plant materials was comparable to one another. Temperature at maximum devolatilization, T_{max}, for these two legumes ranged between 295 and 343°C. This range was lower than those values for pine wood at 371°C (Baigini et al., 2006), rice husk at 357°C (Biagini et al., 2008), and corn stover near 360°C (Kumar et al., 2008).

Table 5. Devolatilization characteristics at various months after planting (MAP) of sunn hemp (SH) and cowpeas (CP)

Year	Legume	MAP	T_{on} [a] °C	T_{max} [b] °C	T_p [c] °C	VM_p [d] $wt\%_{db}$	VM_s [e] $wt\%_{db}$
2004	CP	1	200	316	359	44.4	8.8
		2	219	323	360	49.3	20.1
	SH	1	211	328	356	41.3	1.0
		2	229	332	358	47.0	12.9
		3	223	335	361	54.5	29.5
2006	CP	1	206	310	350	43.7	11.6
		2	208	296	352	45.6	21.1
		3	205	295	356	49.0	26.3
	SH	1	211	323	359	48.1	13.9
		2	213	338	360	52.1	21.2
		3	221	343	365	50.7	17.9

[a] Onset temperature corresponded to a weight loss of 5%db of the final weight loss; [b] temperature at maximum devolatilization; [c] Temperature at end of primary devolatilization stage; [d] Volatile matter removed during primary devolatilization stage; [e] Volatile matter removed during secondary devolatilization stage.

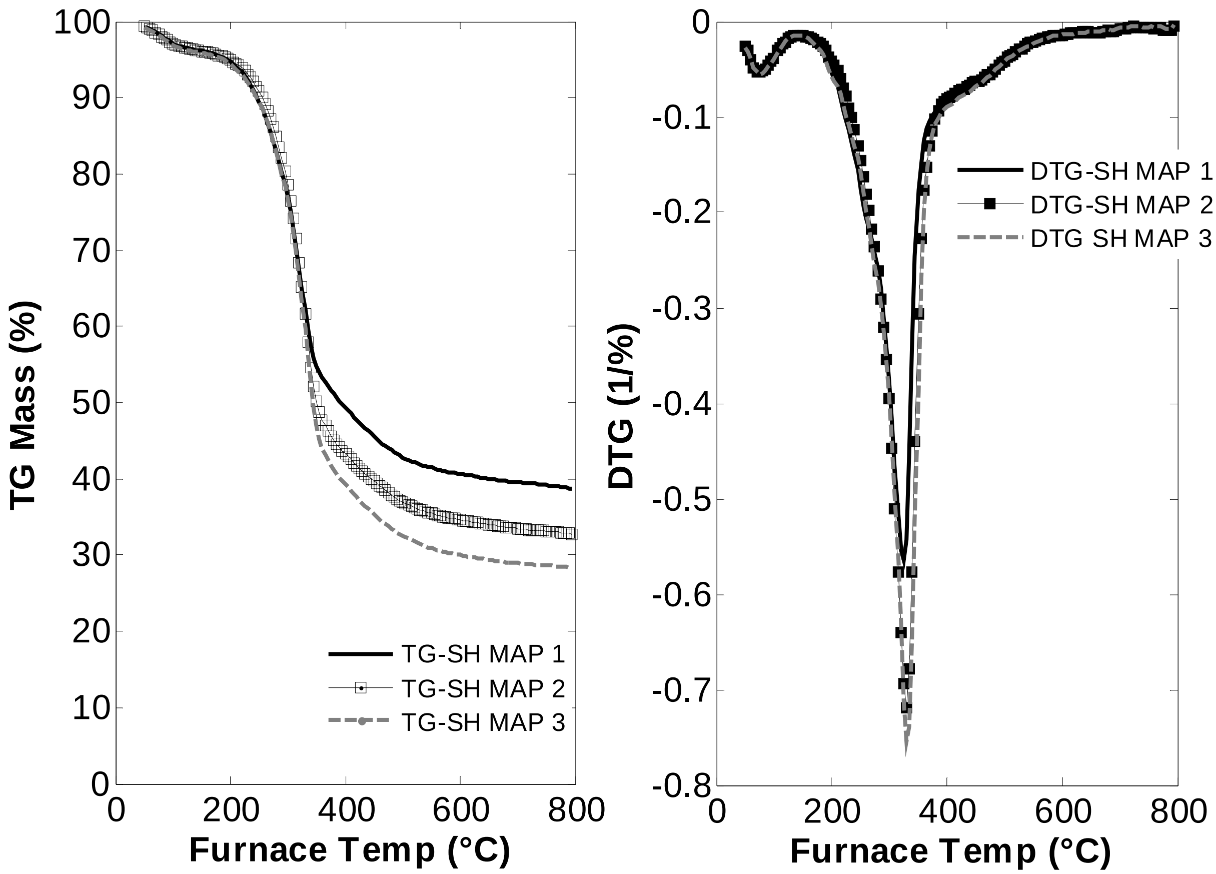

Figure 4. Thermogravimetric characterization of the pyrolysis of sunn hemp (SH) at various months after planting (MAP). (TGA Method: 40 – 800°C; 20 °C min^{-1}; N_2 atmosphere)

Conclusion

In addition to its use as an N-fertilizer source, sunn hemp (*Crotolaria juncea*) is a fast growing, high biomass yielding, tropical legume lending itself to become a suitable southeastern bioenergy crop. When comparing this legume to another commonly grown summer legume—cowpeas, sunn hemp was superior in biomass yield (kg ha^{-1}) and subsequent energy yield (GJ ha^{-1}). Interlinked with energy yield, the sunn hemp energy content (MJ kg^{-1}) at the greatest maturity sampled was 19.0 MJ kg^{-1}. This was 6% greater than that of cowpeas. Despite sunn hemp having a greater amount of ash, sunn hemp concentration of nutrients was lower in some cases of minerals (K, Ca, Mg, S) known to influence thermochemical conversion process. Pyrolytic degradation of both legumes revealed that sunn hemp began to degrade at higher temperatures as well as release more volatile matter. This volatile matter would be amenable to downstream conversion processes to generate either heat or synthetic fuels.

Acknowledgements

The authors are grateful to Cody Alexander, Ashley Kelly, Jerry Martin II, Ernie Strickland, and Don Watts for help with sample collection, preparation, and analyses.

Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

References

ASTM. 2006. Petroleum Products, Lubricants, and Fossil Fuels: Gaseous Fuels; Coal and Coke. W. Conshohocken, PA: ASTM International.

Biagini, E., F. Barontini, and L. Tognotti. 2006. Devolatilization of biomass fuels and biomass components studied by TG/FTIR technique. *Ind. Eng. Chem. Res.* 45: 4486-4493.

Biagini, E., A. Fantei, and L. Tognotti. 2008. Effect of the heating rate on the devolatilization of biomass residues. *Thermochimica Acta*. 472: 55 – 63.

Bauer, P.J., D.M. Park, and B.T. Campbell. 2009. Cotton Production in Rotation with Summer Legumes. *J. Cotton Sci*. (In review).

Boateng, A.A., D.E. Daugaard, N.M. Goldberg, and K.B. Hicks. 2007. Bench-scale fluidized-bed pyrolysis of switchgrass for bio-oil production. *Ind. Eng. Chem. Res.* 46: 1891-1897.

Cantrell, K.B., K.C. Stone, P.G. Hunt, K.S. Ro, M.B. Vanotti, and J.C. Burns. 2009. Bioenergy from coastal bermudagrass receiving subsurface drip irrigation with advance-treated swine wastewater. *Biores. Technol.* 100(13): 3285-3292.

Fisher, T., M. Hajaligol, B. Waymack, and D. Kellogg, Pyrolysis behavior and kinetics of biomass derived materials. *J. Anal. Appl. Pyrolysis*. 62: 331-349.

Kumar, A., L. Wang, Y.A. Dzenis, D.D. Jones, and M.A. Hanna. 2008 Thermogravimetric characterization of corn stover as gasification and pyrolysis feedstock. *Biomass Bioenerg.* 32: 460-467.

Mansoer, Z., D.W. Reeves, and C.W. Wood. 1997. Suitability of sunn hemp as an alternative late-summer cover crop. *Soil Sci. Soc. Am. J*. 61:246-253.

Raveendran, K., Ganesh, A., 1996. Heating value of biomass and biomass pyrolysis products. *Fuel.* 75, 1715-1720.

Raveendran, K., Ganesh, A., Khilar, K.C., 1995. Influence of mineral matter on biomass pyrolysis characteristics. *Fuel*. 74, 1812-1822.

Ro, K.S., K. Cantrell, D. Elliott, and P.G. Hunt. 2007. Catalytic wet gasification of municipal and animal wastes. *Ind. Eng. Chem. Res.* 46: 8839-8845.

Williams, P.T., Horne, P.A., 1994. The role of metal salts in the pyrolysis of biomass. *Renew. Energ.* 4, 1-13.